Microwave plasma based single-step method for generation of carbon nanostructures

A. Dias[1], E. Tatarova[1], J. Henriques[1], C. C. Luhrs[2], J. Phillips[2]and C. M. Ferreira[1]

[1] *Institute of Plasmas and Nuclear Fusion, Instituto Superior Técnico, Technical University of Lisbon, Portugal*
[2] *Mechanical and Aerospace Engeneering, Naval Postgraduate School, Monterey, CA 93943, U.S.A.*

Plasma environments constitute powerful tools in materials science due to their operation as thermal and chemical reactors. A microwave, atmospheric argon plasma driven by surface waves has been used for synthesizing carbon nanostructures by passing vaporized ethanol through the plasma. Graphene sheets and carbon nanoparticles have been selectively synthesized through the control of the outlet plasma stream temperature.

1. Introduction

Nowadays, carbon based two-dimensional (2D) nanostructures are one of the ongoing strategic research areas in science and technology. Graphene, an atomically thin sheet of carbon atoms tightly packed in a 2D honeycomb lattice, possesses many extraordinary properties and its potential applications include electronic devices, transparent conductive films, mechanical devices, chemical sensors, spintronic devices. Moreover, it shows enormous potential as a storage material for energy applications. Graphene of highest quality can be obtained by mechanically exfoliating highly oriented pyrolytic graphite but the fact that the approach is not scalable for commercial applications has driven a search for alternative techniques to obtain high yields of clean and highly ordered graphene [1]. Hereof, it is well recognized that the unique chemically active plasma environment provides suitable conditions to dissociate/atomize molecules in order to synthesize unique structures in ways that are not otherwise possible [2]. Many applications exploit the ability of plasmas to break down complex molecules considering that plasma systems provide simultaneously high temperatures and a highly reactive environment. Many of the current plasma techniques aimed at synthesizing carbon nanostructures involve plasma enhanced chemical vapor deposition (PECVD). However, the synthesis of graphene by CVD requires multiple processing steps, such as wet-etching and micro-fabrication, to obtain transferable sheets [1]. A plasma based method to synthesize substrate free, *i.e.*, "free–standing" graphene at ambient conditions has been demonstrated in [2-4]. The results demonstrate that clean and highly ordered graphene sheets similar in quality to those obtained through mechanical exfoliation can be synthesized by using microwave plasmas. The quality of the graphene sheets created is controlled by the amount of precursors in the feeding gas stream and the microwave power and background gas used.

In the present work, a microwave atmospheric plasma driven by surface waves has been used to generate various carbon nanostructures, including graphene sheets and nanospheres. The method is based on sending ethanol droplets through a microwave argon plasma environment, where decomposition of ethanol molecules takes place and carbon atoms are created. These atoms recombine subsequently in the outlet plasma stream to form nanostructures that are collected by nylon membrane filters. Since the temperature of the outlet plasma stream determines the nucleation conditions a cryostatic system has been used to fix the wall temperature in the nucleation zone of the plasma reactor. In fact, the type of nanostructures created strongly depends on the outlet plasma stream temperature as the obtained results demonstrate.

2. Experimental setup and conditions

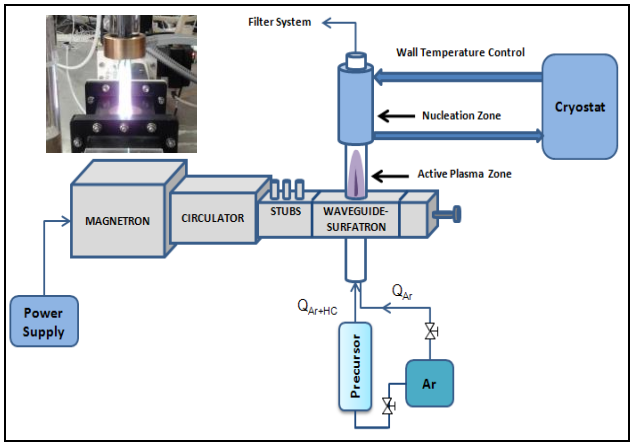

Figure 1. Experimental setup

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14. ABSTRACT
Plasma environments constitute powerful tools in materials science due to their operation as thermal and chemical reactors. A microwave, atmospheric argon plasma driven by surface waves has been used for synthesizing carbon nanostructures by passing vaporized ethanol through the plasma. Graphene sheets and carbon nanoparticles have been selectively synthesized through the control of the outlet plasma stream temperature.

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A surfatron-based setup is used to create a surface wave induced microwave plasma [5]. The microwave power is provided by a 2.45 GHz generator (Sairem), whose output power was varied from 400 to 900W. The generator is connected to a waveguide (WR-340) system, which includes an isolator, directional couplers, a 3-stub tuner and a waveguide surfatron as the field applicator. The system is terminated by a movable short-circuit. The discharge takes place inside a quartz tube with internal and external radii of 7.5 mm and 9 mm, respectively, which is inserted vertically and perpendicularly to the waveguide wider wall. A second quartz tube with internal and external radii of 1.5 and 2.5 mm, respectively, is used to introduce the vaporized precursor, *i.e.*, ethanol droplets in the discharge zone. The background argon gas is injected into the discharge tube at flow rates (Φ) varying from 250 to 2000 sccm under laminar gas flow conditions. The precursor partial flux (Φ_{pr}) varies in the range 0.5 to 3.5 sccm. Vaporization is performed at room temperature by passing argon gas through a porous filter, composed of bonded grains of quartz glass immersed in the precursor liquid inside a tank. The total flow passing through the discharge consists in the direct argon flow passing through the large quartz tube plus the combined flows of the argon bubbling in the precursor liquid and the vaporized precursor, passing though the small quartz tube. Gas flow rates are controlled by a MKS 247 Readout coupled to two MKS flow meters. The outlet gas stream temperature was actively controlled by a cryostat system. The cooling/heathing fluid circulates, with a constant flow rate, between the cryostat and a tubular heat exchanger as shown in Fig. 1. The heat exchanger consists of an external pyrex tube, with internal and external radii of 36 and 42 mm, concentrically aligned with the outer discharge quartz tube; the wall of the quartz tube is the heat transfer surface. The heat exchanger is placed immediately after the end of the discharge zone. The nanostructures were captured by a membrane filter system coupled to an Edwards BS2212 two-stage vacuum pump (see Fig. 1). The samples obtained have been analysed by transmission electron microscopy (TEM, JEOL 2010) and Raman spectroscopy (LabRAM HR Evolution).

3. Experimental results

The microwave plasma reactor contains two zones. One is the discharge zone, where the ethanol molecules are thermally decomposed into simple atoms and molecules (C, H, O, H2, C_2, O_2, CO, CO_2) due to the high temperature (~ 3000 ^oK). The axial gas flow transports the carbon atoms to the second aggregation zone, *i.e.*, the outlet gas stream, where thermally assisted kinetic processes of nucleation and growth take place. By externally forced cooling/heating, these processes can be ruled in a way to create nanostructures with different designs, *i.e.*, particles or sheets. The evolution in the structure of the synthesized nanostructures with externally forced cooling/heating are shown in Figs. 2,3. Nearly spherical particles with diameters in the range of 10 to 15 nm (usually referred in the literature as fullerene soot) are formed at low (0 ^oC - 10 ^oC) temperatures (Fig. 2). At the temperature of 18 ^oC there is a mix of particles and sheets (Fig. 3a) while at 25 ^oC graphene sheets are the only nanostructures present (Fig. 3b). It should be mentioned that the type of nanostructures created depends also on the precursor and background argon fluxes as shown in [2,3].

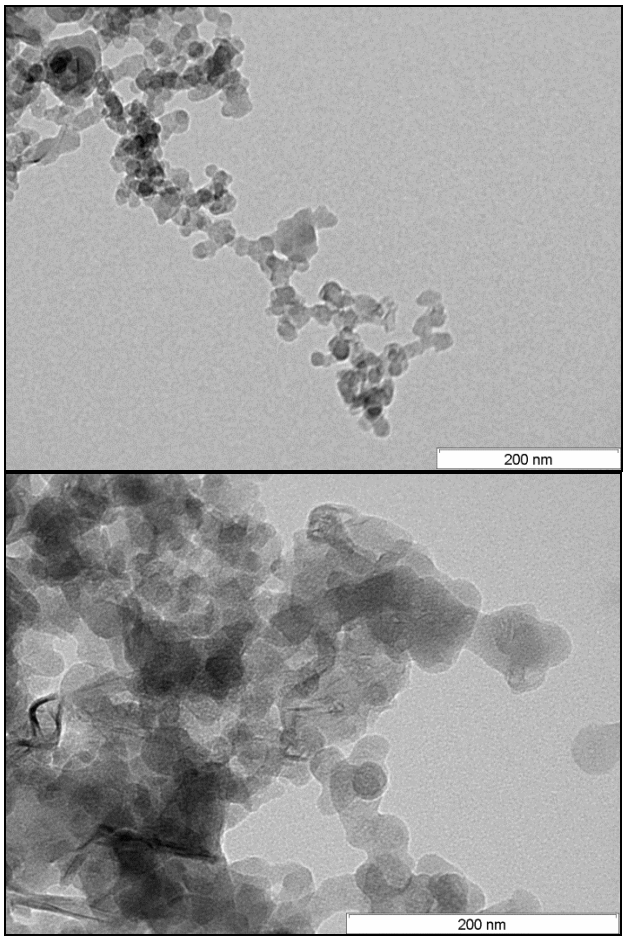

Figure 2. TEM images of the nanostructures obtained at P = 500 W, Φ =250 sccm, Φpr = 0.6 sccm and wall temperature (a) T = 0 ^oC (b) T = 10 ^oC.

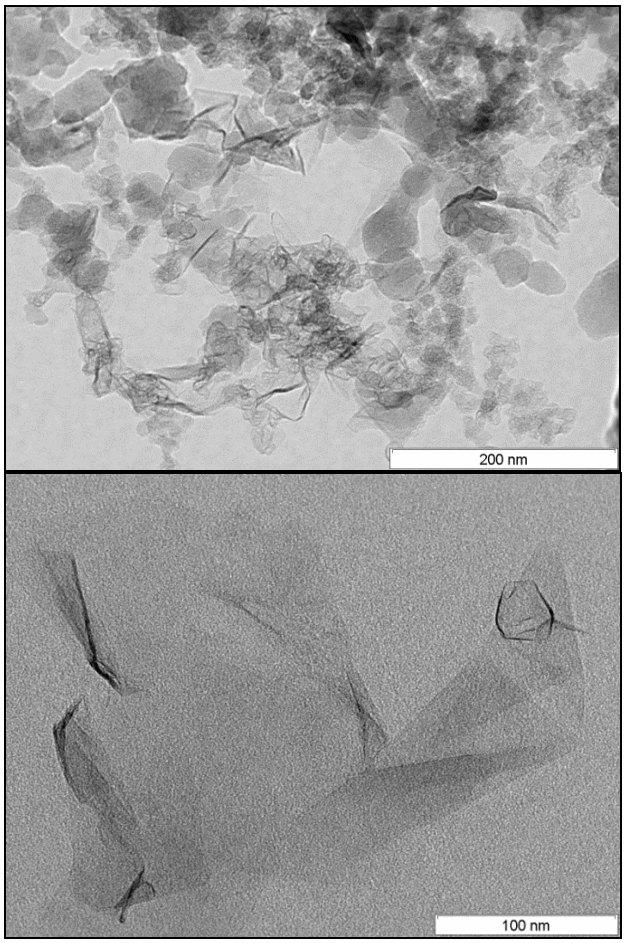

Figure 3. TEM images of the nanostructures obtained at P = 500 W, Φ =250 sccm, Φpr = 0.6 sccm and wall temperature (a) T = 18 ^{o}C (b) T = 25 ^{o}C.

As seen in Fig. 3b, there are both homogeneous and less transparent areas in the synthesized sheet. The latter can be attributed to the folding and overlapping of the sheets. The Raman spectrum of the graphene sheets created for a wall temperature T = 100 ^{o}C is shown in Fig. 4.

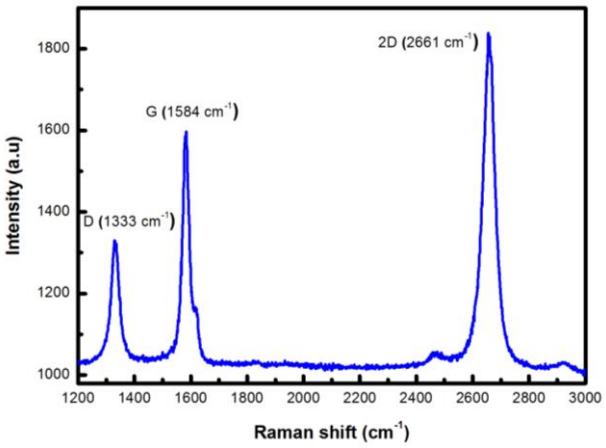

Figure 4. Raman spectrum obtained at: T = 100 ^{o}C; P = 900 W; Φ=250 sccm; Φ_{pr} =0.6 sccm.

The most prominent feature in the Raman spectrum of graphene is the 2D peak, whose position, shape and intensity are used to distinguish between single-layer, bi-layer and multi-layer graphene. As seen in this figure, the sheet exhibits a sharp 2D peak at about 2661 cm^{-1}. Taking into account the ratio between the G and 2D peak intensities, the obtained results can be interpreted as an indication of single-layer graphene. The appearance of the D peak at ~1333 cm^{-1} and the small shoulder of the G peak at ~1620 cm^{-1} can be considered as a result of structural disorders in the created sheets.

4. Acknoledgment

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